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Supporting Information

Theoretical Insights into Promotion Effect of Alkali Metal Cations on Electroreduction Mechanism of CO_2 into C_1 Products at Cu(111)/H_2O Interface

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1. Computational Details

1.1 Surface and Solvation Model

The closed-packed Cu(111) single-crystal surface is generally chosen as representative crystal plane for both experimental and theoretical studies due to its high selectivity to CO_2 electroreduction into C_1 products. Considering complexity of real CO_2 electroreduction systems, the aqueous-phase environment is included. Our present solvation model is on the basis of the previous experimental and theoretical studies on structure and orientation of H_2O molecules,[1-3] where 12 explicit H_2O molecules with two relaxed bilayer structures were employed to simulate solvation effect in order to better model interactions between solvent and adsorbates and decrease size of the simulated systems as much as possible. Considering the coverage is 2/3 of H_2O monolayer, therefore, a (3x3) Cu(111) slab model with nine metal atoms per layer and theoretical equilibrium lattice constant of 3.66 Å by using four metal layers was created. Alkali metals Na and Cs with different atomic size are incorporated into Cu(111)/H_2O interface model in this paper. Alkali metal cations have been hypothesized to adsorb to the electrode surface or interact with surface-adsorbed species non-covalently.[4, 5] However, surface X-ray scatting data have suggested alkali metal cations to be solvated and not adsorbed at the electrode surface.[6] In this paper, alkali metals Na and Cs are initially adsorbed on Cu(111) surface. However, alkali metals are spontaneously solvated and not adsorbed on Cu(111) after geometry

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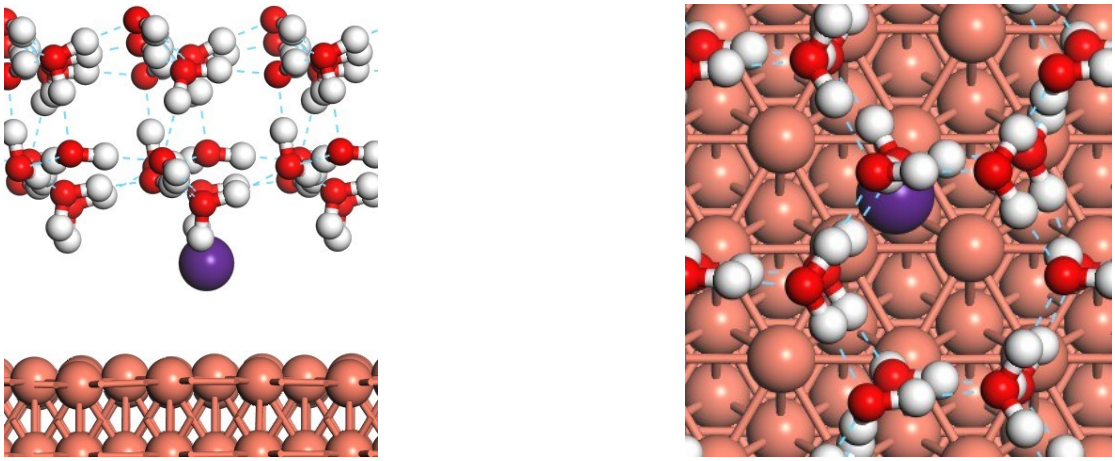
relaxation and optimization, confirming experimental observations, as can be seen in Fig. S1.



(a) (b)

Fig. S1. The Solvation Model Containing Alkali Metal Cations on Cu(111): (a) Side View; (b) Top View.

1.2 CO Coverage-Dependent Equilibrium Potential

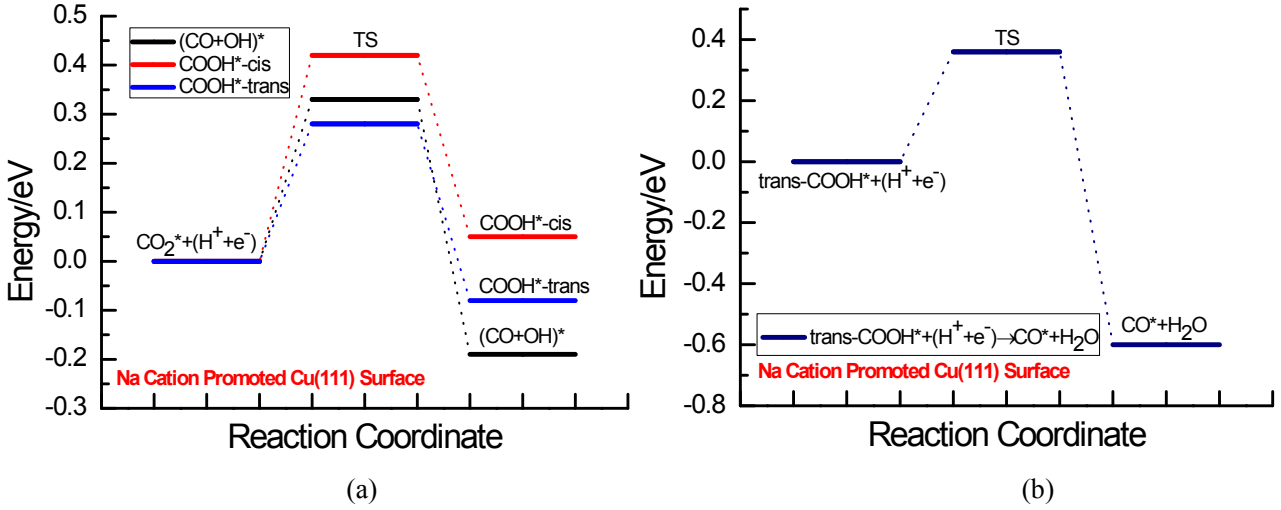
As elaborated in our recent study,[7] the differential adsorption energy of CO, $\Delta E(\theta)$ exhibits reasonable linear dependence on θ_{CO} on Cu(111). Linearly fitting $\Delta E(\theta)$~θ_{CO} data to straight line enables us calculate $\Delta E(\theta)$ at any θ_{CO}. Thus, the linear relationships between CO coverage (θ_{CO}) and the calculated equilibrium potentials (U) can be obtained on Cu(111). It can be observed that more CO coverage will lead to more negative equilibrium potential for CO_2 electroreduction, suggesting that overpotential may mainly originate from the adsorbed CO on Cu electrodes. The calculated thermodynamical equilibrium potential is *ca*. 0.27 V (*vs*. RHE) when θ_{CO} is closely zero, which is comparable with thermodynamical equilibrium potential of 0.17 V (*vs*. RHE) for CO_2 electroreduction from literature and confirm the reasonability of the present theoretical model to some degree.[8] Our recent study focused on CO adsorption with low coverage of 1/9 ML on clean Cu(111) and calculated equilibrium potential is *ca*. 0.14 V (*vs*. RHE),[7] corresponding to the condition of low overpotential compared with thermodynamical equilibrium potential when θ_{CO} is closely zero (*ca*. 0.13 V). In this paper, alkali metals Na with smaller atomic size and Cs with relatively larger atomic size are integrated into our recent proposed CO coverage-dependent Cu(111)/H_2O electrochemical interface model, which are used to study influences of alkali metal cations on CO_2 electroreduction mechanisms in aqueous electrolyte.

1.3 Computational Parameters

All calculations were performed in the framework of DFT using the generalized gradient approximation

of Perdew–Burke–Ernzerhof exchange correlation functional.[9] Ultrasoft pseudopotentials were employed to describe the nuclei and core electrons and a plane-wave basis set was used to self-consistently solve the Kohn-Sam equations.[10] A kinetic energy cutoff of 30 Ry and a charge-density cutoff of 300 Ry were used to make basis set finite. The smearing technique of Methfessel-Paxton was employed to treat the Fermi surface with a smearing parameter of 0.02 Ry.[11] All DFT calculations were carried out by the PWSCF codes included in Quantum ESPRESSO distribution.[12] A (3×3×1) uniformly shifted k-mesh for (3×3) supercell were used to implement Brillouin-zone integrations with the special-point technique. A vacuum layer of 16Å was placed above the top layer of slab, which is sufficiently large to ensure that the interactions are negligible between repeated slabs. The Cu atoms in the bottom two layers are fixed at the theoretical bulk positions, whereas the top two layers and adsorbates involving solvent are allowed to relax. Structural optimization was performed until the Cartesian force components acting on each atom were brought below 10^{-3} Ry/Bohr and the total energy was converged to within 10^{-5} Ry. The saddle points and minimum energy paths (MEPs) were located by using the climbing image nudged elastic band (CI-NEB) method.[13, 14] Zero point energy (ZPE) corrections were applied into calculations of the activation and reaction energies from MEP analysis, in which density functional perturbation theory was used to study the vibrational properties.[15] The ZPEs were calculated using the PHONONS code that contained in the Quantum ESPRESSO distribution.[12]

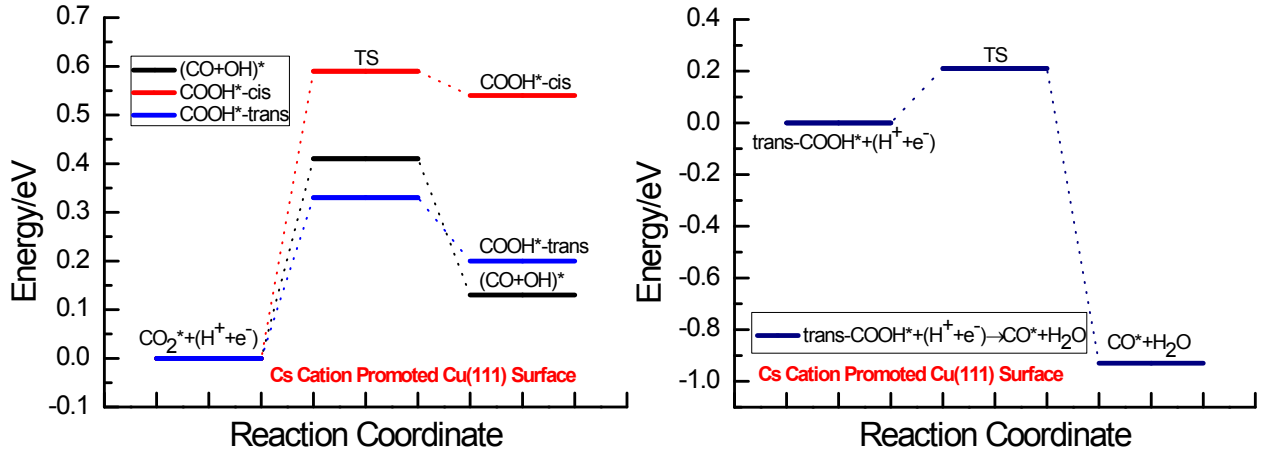
2. Minimum Energy Pathway (MEP) Analysis



(a) (b)

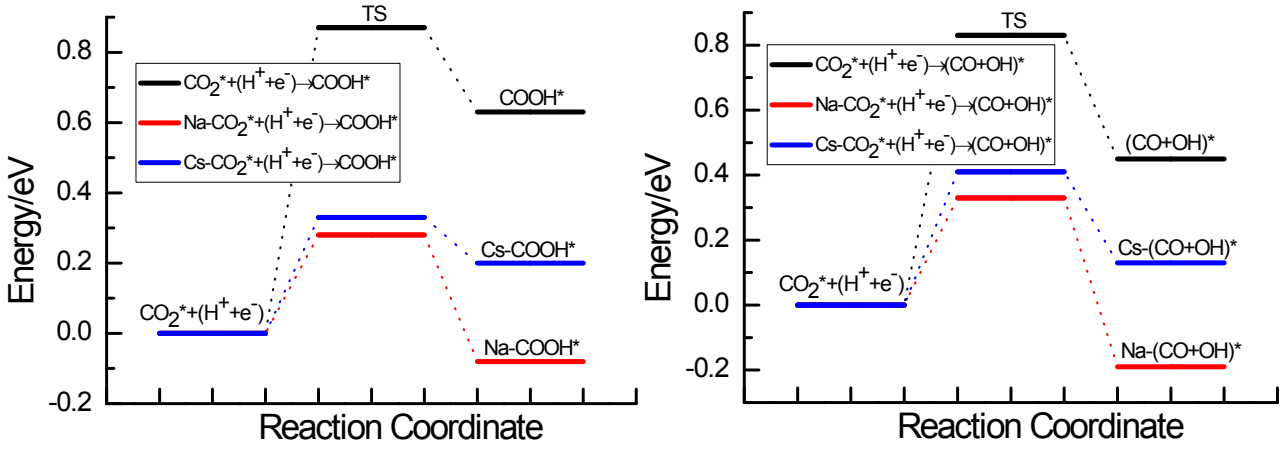
Fig. S2. The MEP analysis of (a) the first elementary step of CO_2 electroreduction and (b) subsequent *trans*-COOH electroreduction into CO and H_2O at Na cation promoted Cu(111)/H_2O interface (an asterisk * indicates

adsorption to the Cu surface)



(a) (b)

Fig. S3. The MEP analysis of (a) the first elementary step of CO_2 electroreduction and (b) subsequent *trans*-COOH electroreduction into CO and H_2O at Cs cation promoted Cu(111)/H_2O interface (an asterisk * indicates adsorption to the Cu surface)



(a) (b)

Fig. S4. The MEP analysis of (a) CO_2 electroreduction into COOH species; (b) CO_2 electroreduction into CO intermediate at clean, Na and Cs cations promoted Cu(111)/H_2O interface (an asterisk * indicates adsorption to the Cu surface)

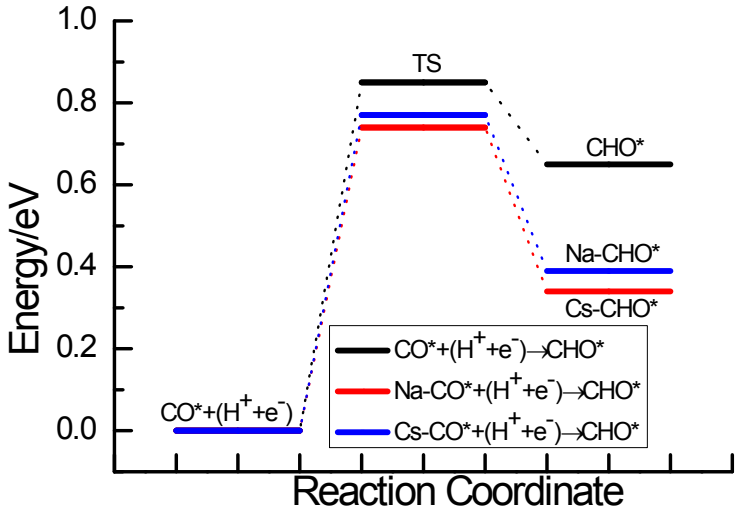


Fig. S5. The MEP analysis of CO electroreduction into CHO species intermediate at clean, Na and Cs cations promoted Cu(111)/H_2O interface (an asterisk * indicates adsorption to the Cu surface)

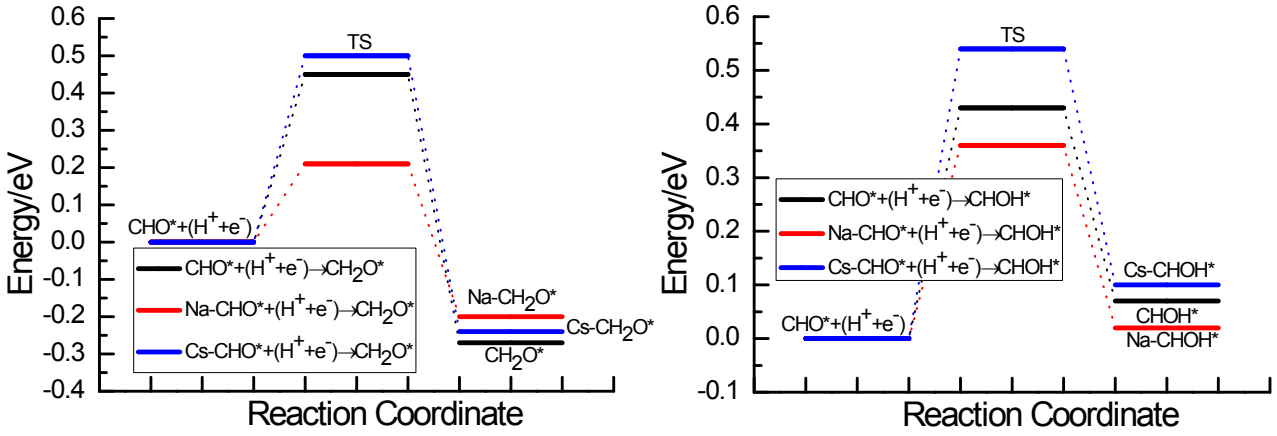
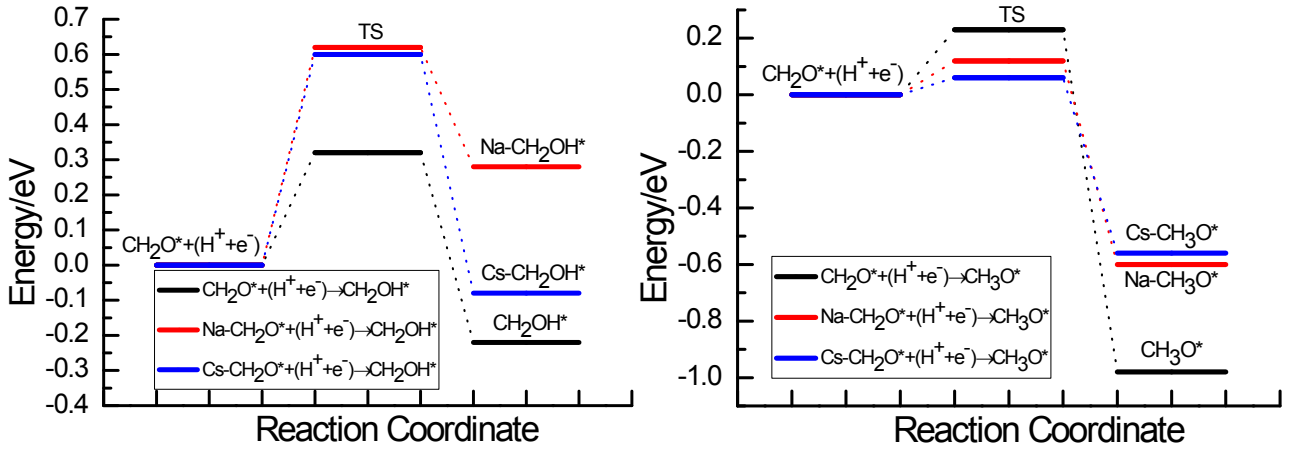
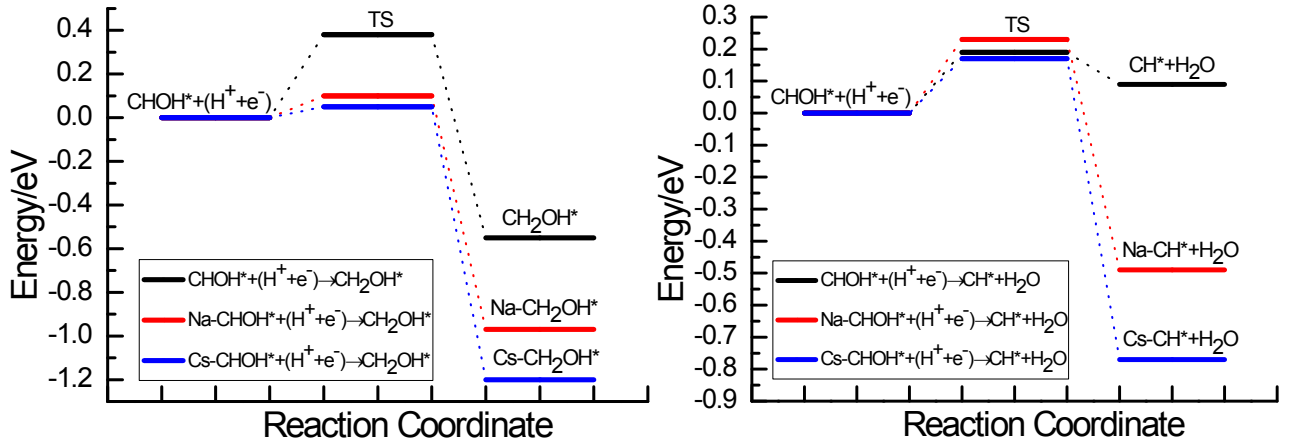


Fig. S6. The MEP analysis of (a) CHO electroreduction into CH_2O species; (b) CHO electroreduction into CHOH species at clean, Na and Cs cations promoted Cu(111)/H_2O interface (an asterisk * indicates adsorption to the Cu surface)



(a) (b)

Fig. S7. The MEP analysis of (a) CH_2O electroreduction into CH_2OH species; (b) CH_2O electroreduction into CH_3O species at clean, Na and Cs cations promoted Cu(111)/H_2O interface (an asterisk * indicates adsorption to the Cu surface)



(a) (b)

Fig. S8. The MEP analysis of (a) CHOH electroreduction into CH_2OH species; (b) CHOH electroreduction into CH species along with H_2O formation at clean, Na and Cs cations promoted Cu(111)/H_2O interface (an asterisk * indicates adsorption to the Cu surface)

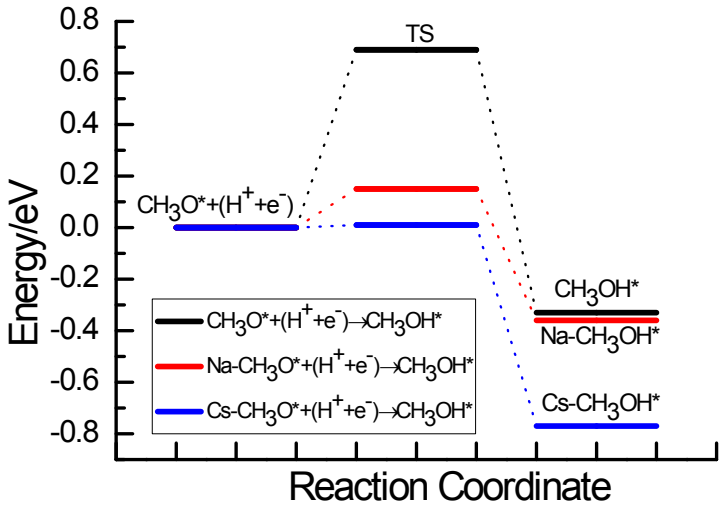
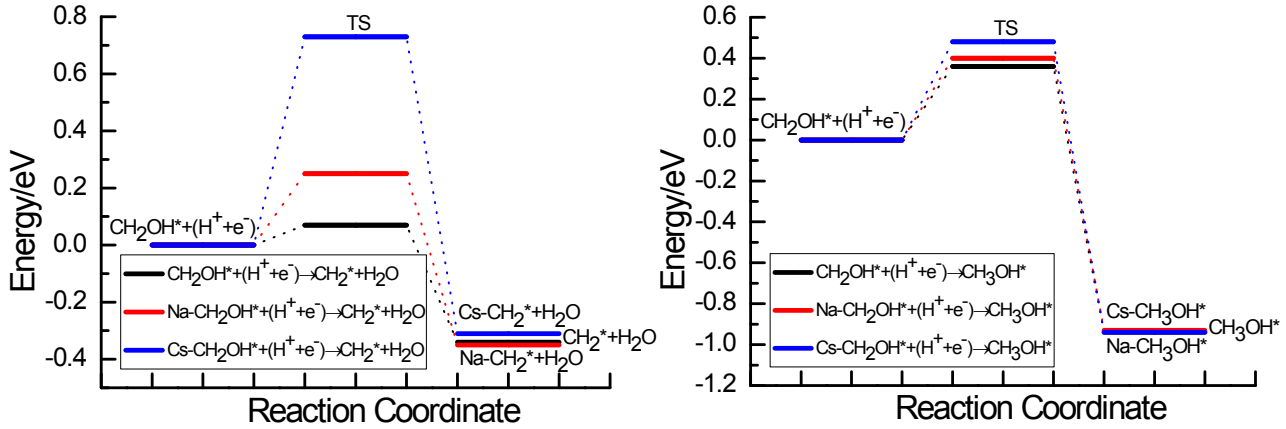
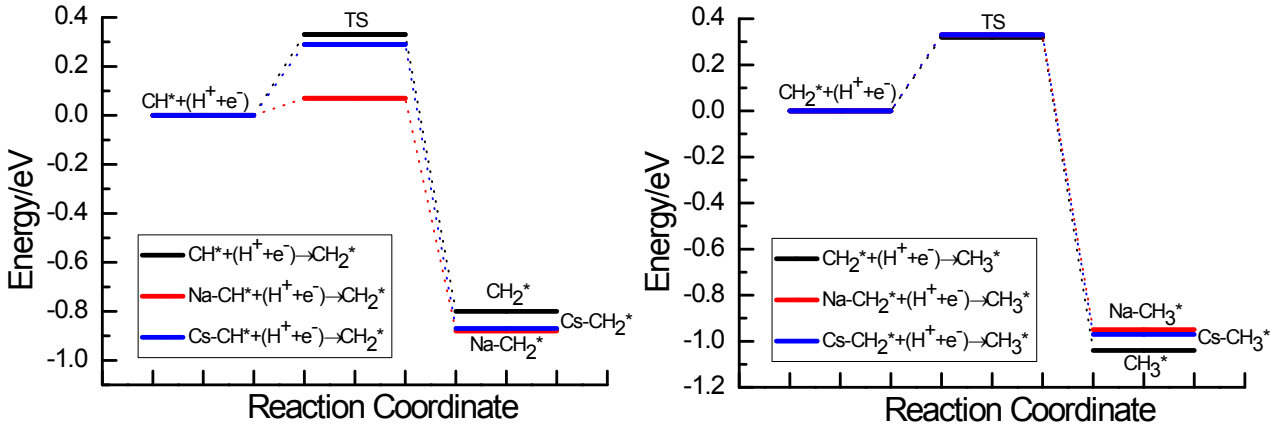


Fig. S9. The MEP analysis of CH_3O electroreduction into CH_3OH product at clean, Na and Cs cations promoted Cu(111)/H_2O interface (an asterisk * indicates adsorption to the Cu surface)



(a) (b)

Fig. S10. The MEP analysis of (a) CH_2OH electroreduction into CH_2 species along with H_2O formation; (b) CH_2OH electroreduction into CH_3OH product at clean, Na and Cs cations promoted Cu(111)/H_2O interface (an asterisk * indicates adsorption to the Cu surface)



(a) (b)

Fig. S11. The MEP analysis of (a) CH electroreduction into CH_2 species; (b) CH_2 electroreduction into CH_3 species at clean, Na and Cs cations promoted Cu(111)/H_2O interface (an asterisk * indicates adsorption to the Cu surface)

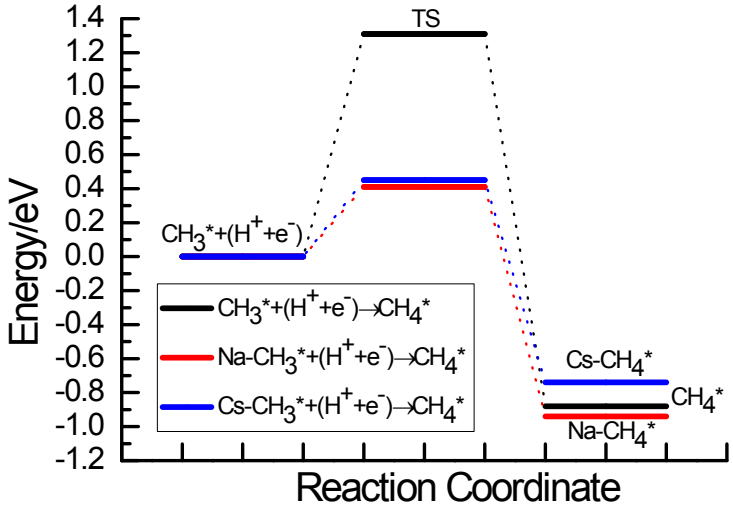


Fig. S12. The MEP analysis of CH_3 electroreduction into CH_4 product at clean, Na and Cs cations promoted Cu(111)/H_2O interface (an asterisk * indicates adsorption to the Cu surface)

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